DERIVATION OF THE EQUIPARTITION THEOREM

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Abstract

The equipartition theorem (of statistical thermal physics) is stated and derived, with some associated discussion.

When one begins the study of statistical mechanics one comes across the following facts, among others:

1. For a one-dimensional harmonic oscillator of frequency ω, the heat capacity at high temperature tends to the value $k_{\rm B}$, independent of the value of ω.
2. For a rigid rotator with an axis of symmetry (such as a diatomic molecule), the heat capacity at high temperature tends to the value $k_{\rm B}$, independent of the value of I, the moment of inertia.
3. For a monatomic gas in a box of volume V, but otherwise free to move, the heat capacity tends to $(3/2)k_{\rm B}$ per particle at high temperature, independent of the mass and other properties.

It is natural to ask whether these can be seen as examples of a single idea. They can:

> **Equipartition theorem**. Each independent quadratic term in the Hamiltonian makes a contribution $\frac{1}{2}k_{\rm B}T$ to the mean internal energy in thermal equilibrium when the associated motion is highly excited.

To understand the statement of the theorem, we can use the above examples.

1. Harmonic oscillator in one dimension: Hamiltonian

   $$H(x, p_x) = \frac{p_x^2}{2m} + \frac{1}{2}m\omega^2 x^2 \tag{1}$$

   a term quadratic in p_x and a term quadratic in x, hence two such terms. Therefore the theorem asserts that the internal energy will be $2 \times \frac{1}{2}k_{\rm B}T = k_{\rm B}T$ at high temperature.
2. Rigid rotator in 3 dimensions, with a symmetry axis:

   $$H(\theta, \phi, L_1, L_2) = \frac{L_1^2}{2I} + \frac{L_2^2}{2I} \tag{2}$$

   where L_1 and L_2 are the angular momenta for rotations about the two directions orthogonal to the symmetry axis. Hence there are two independent quadratic terms, so the theorem asserts that the internal energy will be $2 \times \frac{1}{2}k_{\rm B}T = k_{\rm B}T$ at high temperature.

3. Translational motion for free particles

$$H(x, y, z, p_x, p_y, p_z) = \frac{p_x^2}{2m} + \frac{p_y^2}{2m} + \frac{p_z^2}{2m} \tag{3}$$

Three terms, so the internal energy is $(3/2)k_{\rm B}T$ at high temperature.

In the above examples we expressed the Hamiltonian in each case as a function of its proper variables, which are position variables and the associated canonical momenta. It is important to note that whereas translational kinetic energy can be written $p^2/2m$ where p is the total momentum, there are nonetheless three terms in the Hamiltonian, not one, because we have to count the *independent* motions. A similar remark applies to angular momentum and L^2.

The proof of the theorem has one main ingredient which we assume as an axiom. We shall present some examples at the end to show how the axiom is underpinned by quantum theory:

> *Axiom.* Mutually orthogonal quantum states fill phase space at a uniform density on average.

The phrase 'on average' here means after averaging over a region containing some moderately (or very) large number of states. *Phase space* here is position-momentum space. For motion of a single particle in D dimensions, phase space is a $2D$-dimensional abstract mathematical space, each point of which specifies a state of motion by giving a position and momentum. The idea of filling phase space at uniform density is that if we examine a region of phase space containing a large number of quantum states, we shall find the number of mutually orthogonal states is proportional to the volume of the region.

1 Proof

1.1 First method

We can now prove the equipartition theorem, as follows. We treat a single particle moving in three dimensions in the first instance. Suppose the Hamiltonian of some given system has the form

$$H(x, y, z, p_x, p_y, p_z) = ax^2 + K(y, z, p_x, p_y, p_z) \tag{4}$$

where K accounts for any contributions which do not involve x. In thermal equilibrium we have

$$\langle ax^2 \rangle = \sum_i ax_i^2 p_i = \frac{1}{Z} \sum_i ax_i^2 e^{-\beta(ax_i^2 + K_i)} \tag{5}$$

where x_i and K_i refer to the value of x and K, respectively, in the relevant state. Next we assume the temperature is high enough that many terms in the sum contribute significantly, and therefore it can be well approximated by an integral. *Using now the property that mutually orthogonal states are uniformly distributed in phase space*, we find

$$\begin{aligned}
\langle ax^2 \rangle &= \frac{\iiint \iiint ax^2 e^{-\beta ax^2} e^{-\beta K} {\rm d}x{\rm d}y{\rm d}z{\rm d}p_x{\rm d}p_y{\rm d}p_z}{\iiint \iiint e^{-\beta x^2} e^{-\beta K} {\rm d}x{\rm d}y{\rm d}z{\rm d}p_x{\rm d}p_y{\rm d}p_z} && (6)\\
&= \frac{\int ax^2 e^{-\beta ax^2} {\rm d}x}{\int e^{-\beta ax^2} {\rm d}x} && (7)\\
&= \frac{1}{2\beta} \;=\; \tfrac{1}{2} k_{\rm B}T && (8)
\end{aligned}$$

A similar calculation involving a term of the form bp_x^2 would give the same result, and for a sum of terms one would get a sum of integrals in the numerator, leading to a sum of $\frac{1}{2}k_{\rm B}T$ values. Finally, for two or more particles one has to integrate over more variables but the integrals factorize just as in the above and the outcome is unchanged. This completes the proof.

1.2 Proof via energy

It is instructive to prove the equipartition theorem by an alternative (but related) route, as follows. First we note that if the partition function has a power-law dependence on temperature then the internal energy depends linearly on temperature:

$$Z = AT^m \qquad \Rightarrow \quad U = k_{\rm B} T^2 \frac{\partial \ln Z}{\partial T} = m k_{\rm B} T. \tag{9}$$

Also, if the number of states in a range of energy $\mathrm{d}\epsilon$ is $g(\epsilon)\mathrm{d}\epsilon$ then

$$Z = \int_0^\infty e^{-\beta\epsilon} g(\epsilon)\mathrm{d}\epsilon \tag{10}$$

Consider the case where the density of states $g(\epsilon)$ has a power-law dependence on energy. One finds

$$Z \propto \int_0^\infty e^{-\beta\epsilon}\epsilon^r \mathrm{d}\epsilon \;\propto T^{r+1} \tag{11}$$

which is easy to prove by making a change of variable in the integral.

Using the above, we deduce that if the density of states satisfies

$$g(\epsilon) \propto \epsilon^{(n/2)-1} \tag{12}$$

where n is the number of independent quadratic terms in the Hamiltonian, then the equipartition theorem will follow.

It is easy to prove that $g(\epsilon)$ does indeed have the form (12). Let us first consider the case $n = 2$, to get the idea. With two quadratic terms, for example in x and p_x, the states of motion have energy satisfying

$$\epsilon = ax^2 + bp_x^2 \tag{13}$$

where a and b are constants. Therefore the states at a given energy lie on an ellipse in the x–p_x phase space. The area of an ellipse is π times the product of its semi-major and semi-minor axes, giving

$$\text{area } = \pi(\sqrt{\epsilon/a})(\sqrt{\epsilon/b}) \tag{14}$$

Using now the uniform distribution of states per unit area of phase space, we deduce that the number of quantum states of energy between zero and ϵ is

$$N(\epsilon) \propto \text{area} = \pi\epsilon/\sqrt{ab} \tag{15}$$

and therefore

$$g(\epsilon) = \frac{\mathrm{d}N}{\mathrm{d}\epsilon} \propto \epsilon^0. \tag{16}$$

For this example, therefore, $(n/2) - 1 = 0$ in eqn (12) which implies $n = 2$ so the thermal energy is $2 \times \frac{1}{2} k_{\rm B} T = k_{\rm B} T$.

Generalizing now to any number of quadratic terms, we find the states at given energy lie on an n-dimensional ellipsoid in the phase space. The volume of the ellipsoid is proportional to the product of all its principle radii, giving

$$N(\epsilon) \propto \text{volume of ellipsoid} \propto \epsilon^{n/2} \tag{17}$$

from which (12) follows, and hence the equipartition theorem.

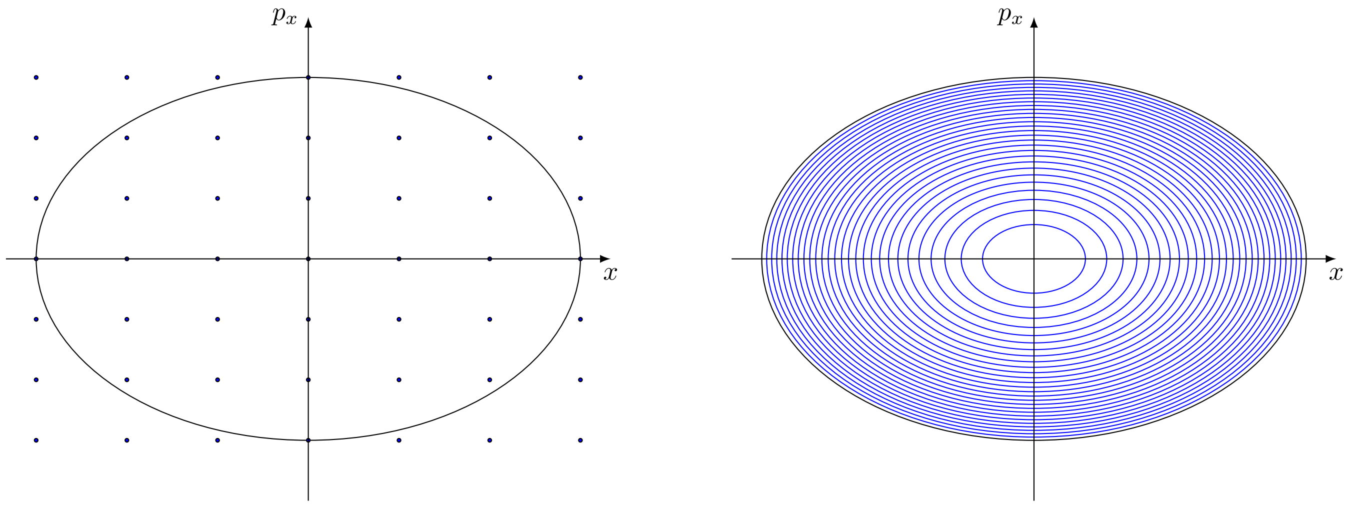

Figure 1: Two ways of counting states in phase space for the harmonic oscillator. States of motion of a given energy lie on an ellipse. On the left we divide the ellipse into rectangular regions with one state per region. On the right we show elliptical rings of equal areas, with one state per ring. The two ways of counting states agree.

2 Areas in phase space

Let us also confirm the uniformity of the areas in phase space occupied by orthogonal quantum states, by examining three examples.

Example 1: the harmonic oscillator. The energy eigenvalues are $(n + 1/2)\hbar\omega$ and the state of energy ϵ falls on an ellipse in phase space. The area of the elliptical ring between one state and the next is

$$\text{area } = \pi(x_0 + \Delta x)(p_0 + \Delta p) - \pi x_0 p_0 \; = \; \pi\,(x_0 \Delta p + p_0 \Delta x) \tag{18}$$

where x_0 and p_0 are the amplitudes of oscillations in x and p, given by

$$\epsilon = \frac{1}{2} m\omega^2 x_0^2 = p_0^2/2m \tag{19}$$

and Δx, Δp are the changes in these quantities from one state to the next:

$$\epsilon + \hbar\omega = \frac{1}{2} m\omega^2 (x_0 + \Delta x)^2 = (p_0 + \Delta p_0)^2/2m \tag{20}$$

By combining the last two equations one finds

$$x_0 \Delta x = \hbar/m\omega \qquad \text{and} \quad p_0 \Delta p = m\hbar\omega \tag{21}$$

Eqn (19) gives $p_0 = m\omega x_0$ so we have $x_0\Delta = \hbar$ and $p_0 \Delta x = \hbar$. Substituting these into (18) we find

$$\text{area } = 2\pi\hbar = h \tag{22}$$

Hence all the rings have the same area, and that area is Planck's constant.

Example 2: particle in an infinite square well. A classical particle moving in a well bounded by hard barriers at $x = 0$ and $x = L$ moves between those barriers at constant momentum, such that a state of given energy lies on a rectangle in phase space, with sides at $x = 0$, $x = L$, $p = \sqrt{2m\epsilon}$ and $p = -\sqrt{2m\epsilon}$. For a quantum particle the momentum values are given by $p = \hbar k$ where $kL = n\pi$ for positive integer n. Hence the change in momentum between one state and the next is

$$\Delta p = \hbar \Delta k = \hbar\pi/L. \tag{23}$$

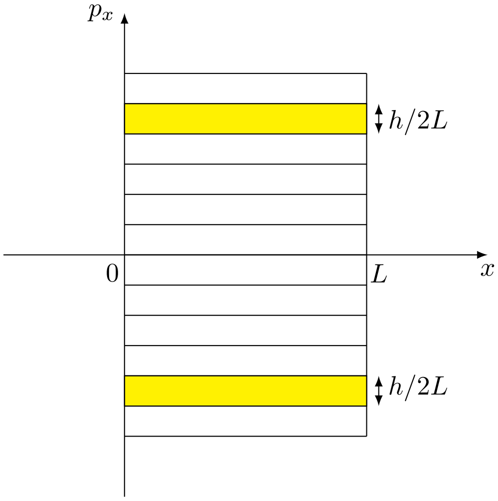

Figure 2: States in phase space for a particle in a box. The pair of filled regions represents a single state.

The difference in area between each rectangle and the next is therefore

$$2(p + \Delta p)L - 2pL = 2\Delta pL = 2\pi\hbar = h \tag{24}$$

where the factor 2 is because the rectangle extends from $-p$ to $+p$. The area agrees with the value found for the harmonic oscillator.

Example 3: rigid rotator (in 3d but with a symmetry axis). For this case we will show that the density of states $g(\epsilon)$ is like that of the oscillator, after averaging over the interval from one eigenvalue to the next. For, the energy eigenvalues are $L(L + 1)\hbar^2/2I$ and the degeneracies are $(2L + 1)$. Consider a given energy level described by L. The energy half way between this one and the one below is $\epsilon_- = L^2\hbar^2/2I$ and the energy half way to the one above is $\epsilon_+ = (L+1)^2\hbar^2/2I$. Therefore when the energy increases from ϵ_- to ϵ_+ the energy changes by $(2L+1)\hbar^2/2I$ and the number of states increases by $(2L + 1)$. Therefore the density of states, as a function of energy, is constant.

3 Application to gases and crystalline solids

Most metallic elements and monatomic crystalline solids have a molar heat capacity of about $3R$ at room temperature, where $R = N_\mathrm{A} k_\mathrm{B}$ is the molar gas constant. Solids such as silver bromide and sodium chloride have a molar heat capacity of about $6R$ at room temperature. These observations can be understood by arguing that at room temperature the heat capacity of these materials is mainly owing to vibrations of the atoms in the crystalline lattice. With N atoms there are $3N$ normal modes of vibration in three dimensions. If all these normal modes are well excited then the equipartition theorem predicts $C = 3Nk_\mathrm{B}$, which gives the observed values of $3R$ when $N = N_\mathrm{A}$ and $6R$ when $N = 2N_\mathrm{A}$ (in a mole of NaCl there is a mole of Na atoms and a mole of Cl atoms and therefore $2N_\mathrm{A}$ atoms altogether). A substance such as diamond, with its high Young's modulus, has normal mode frequencies extending to higher values. Consequently it has a lower molar heat capacity at room temperature because the vibrations are not fully excited.

The heat capacity of a gas of diatomic molecules has the generic form shown in figure 3. At low temperatures the molar heat capacity is $(3/2)R$, reflecting the three translational degrees of freedom giving the kinetic energy of translational motion. At intermediate temperatures there is also rotation, which introduces two more independent quadratic contributions to the Hamiltonian of each molecule, therefore increasing the molar heat capacity by R (two lots of $(1/2)N_\mathrm{A} k_\mathrm{B}$) once the rotation is fully excited. At higher temperatures there is also vibration along the line separating the nuclei. This is a one-dimensional harmonic motion, described by two more quadratic terms (p_r^2 and r^2, where r is the relative coordinate) and therefore contributing a further R to the molar heat capacity.

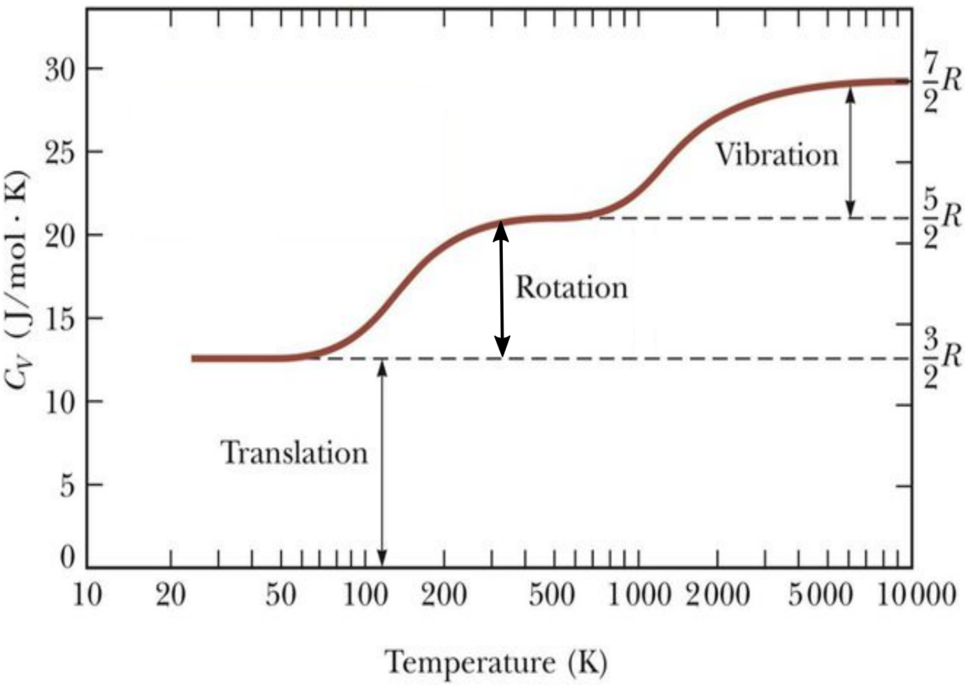

Figure 3: Heat capacity of a diatomic gas. Temperature values are given for hydrogen.

Molecule	T_R (K)	T_v (K)
H_2	87.6	6247
N_2	2.88	3521
O_2	2.08	2256
F_2	1.27	1320
HF	30.2	5957
HCl	15.2	4303
HBr	12.2	3787
CO	2.78	3103
CO_2	0.561	960, 960, 1997, 3380
H_2O	40.1, 20.9, 13.4	2293, 5262, 5404

Table 1: Rotational and vibrational temperature of some example molecules in their electronic ground state.

The rotational temperature is below the boiling point at one atmosphere of pressure for most substances, therefore at one atmosphere the substance is a liquid at the rotational temperature. For such materials as soon as the substance is gaseous its rotation is already fully excited. Hydrogen is the only exception.

3.1 Counting normal modes

We asserted above that a crystalline solid of N atoms has $3N$ normal modes of vibration. This is correct if we assume the solid overall is itself located in a harmonic potential well, or if N is large enough that we don't mind miscounting the normal modes by a number of order 1.

For a molecule which is free to move and rotate, the number of normal modes is smaller than $3N$, where N is the number of atoms in the molecule. For example, for a diatomic molecule ($N = 2$) there is just one normal mode. The general formula is

molecule type	number of normal modes
with rotational symmetry axis	$3N-5$
no rotational symmetry	$3N-6$

These values can be obtained by counting the coordinates and momenta as follows:

	monatomic	with symmetry	without symmetry
total	6	$6N$	$6N$
translation	6	6	6
rotation	0	4	6
vibration	0	$6N-10$	$6N-12$

For example, the 6 translational contributions consist of three coordinates to locate the centre of mass, and 3 momenta to specify the total momentum of the molecule. The rotational contribution consists of the number of angle coordinates required to specify the orientation in space, and an equal number of angular momenta. The vibration contribution accounts for the rest. Each normal mode involves two terms (a position and a momentum) so this leads to the numbers of normal modes as given in the previous table. For example, the CO_2 molecule, which has a symmetry axis, has 4 normal modes of vibration, and the H_2O molecule, which has no symmetry axis, has 3 normal modes of vibration.

4 Generalized equipartition theorem

By using a power series expansion of the Hamiltonian, or otherwise, one can readily show that, in thermal equilibrium at high temperature,

$$\left\langle x_i \frac{\partial H}{\partial x_i} \right\rangle = k_{\mathrm{B}} T \tag{25}$$

where x_i is any one of the coordinates or momenta in terms of which the Hamiltonian is expressed. For example, if there is a term in H of the form ax^q for some power q then we find $\langle qax^q \rangle = k_{\mathrm{B}}T$ and therefore such a term contributes a mean energy $k_{\mathrm{B}}T/q$.

Also, by generalizing the method of Section 1.2, it is easy to prove that if the density of states has the form $g(\epsilon) \propto \epsilon^r$ for some power r (not necessarily integer), then at high temperature $U = (r+1)k_{\mathrm{B}}T$. By combining this with (25) one can show (exercise) that for any Hamiltonian of the form

$$H = \frac{p_x^2}{2m} + ax^q \tag{26}$$

(for example, a particle moving in a power-law potential well in one dimension), the density of states at high energy must be of the form

$$g(\epsilon) \propto \epsilon^{(1/q)-(1/2)}. \tag{27}$$

5 Exercises

1. Estimate the specific heat capacities of silver bromide and of niobium at room temperature. [Relative atomic masses of Ag, Br, Nb are 107.87, 79.90, 92.91]
2. Helium gas is confined in a small flat box of dimensions 0.1 × 10 × 10 microns. Sketch the heat capacity as a function of temperature in the range 1 to 100 μK.
3. A particle is confined in a one-dimensional quartic potential well ($V(x) \propto x^4$). Find the heat capacity in the high temperature limit.